Photoreactions of 1-(3-acetoxy or methoxycarbonylmethoxy-2-pyridyl)-2-(pentamethyldisilanyl)ethynes

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Abstract

Photolysis of 1-(3-methoxycarbonylmethoxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **2b** in benzene provides a novel intramolecular cycloaddition product **15** via silacyclopropene intermediate **13** but the photoreaction of 1-(3-acetoxy-2-pyridyl)-2-(pentamethyldisilanyl)-ethyne **2a** in benzene affords 1-(3-acetoxy or 3-hydroxy-2-pyridyl)-2-(trimethylsilyl)ethyne **5** or **6**, respectively, via silacyclopropene intermediate **3** instead of a intramolecular cycloaddition product.
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1. Introduction

The photochemistry of alkynyldisilanes is useful synthetic methods for the highly strained silacyclopropenes and 1-silaallenes [1–4]. These silacyclopropenes react readily with methanol or acetone in the presence of methanol or acetone as trapping agents. Silacyclopropenes also react with unsaturated functional groups such as aldehydes, ketones, styrenes, conjugated terminal acetylenes, benzynes, terminal 1,3-dienes, and conjugated imines to give five-membered cyclic organosilicon products in which C=O, C=C, C≡C or C=N bonds are inserted into the Si–C bond of the silacyclopropene ring [5]. This type of reaction was first reported by Ishikawa et al. in 1977 who investigated the photoreaction of 1-phenyl-2-(pentamethyldisilanyl)ethyne [6]. Since then the photolysis of 1-(trimethylsilylethynyl)-1,1-diphenyl-2,2,2-trimethyldisilane [7], 1-phenylethynyl-2-phenyltetramethyldisilane [8], 1,1-dimesityl-1-trimethylsilylethynyltrimethyldisilane [9], trimethylsilyl(1,1-diphenyltrimethyldisilanyl)acetylene [10], ((trimethylsilyl)ethynyl)pentamethyldisilane [11], pentamethyl(phenylethynyl)disilane [12–14], 1-aryl-4-(pentamethyldisilanyl)buta-1,3-dienes [15–17], 1,4-bis(pentamethyldisilanyl)butadiene [18], 4,4′-bis(pentamethyldisilanylethynyl)biphenyl [19], 1,4-bis(pentamethyldisilanylethynyl)benzene [20], and 1-(*n*-pyridyl)-2-(pentamethyldisilanyl)ethynes (*n* = 2, 3, or 4) [21] has been studied.

In connection with our ongoing studies for the utility of silacyclopropenes or 1-silaallenes as reaction intermediates in organic synthesis of silicon-containing heterocyclic compounds, we have recently found that the photolysis of *ortho*-substituted 1-phenyl-2-(pentamethyldisilanyl)ethynes afforded novel intramolecular photoproducts via silacyclopropene or 1-silaallene intermediates [22–30]. In the last paper of this series, the authors reported on the photoinduced intramolecular reactions of 1-(3-hydroxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne [31], aza analogue of 1-*ortho*-hydroxyphenyl-2-(pentamethyldisilanyl)ethyne [26,27], containing the nitrogen atom in the benzene ring affording novel intramolecular photoproducts via silacyclopropene or 1-silaallene intermediates.

As a logical consequence, in order to investigate whether or not the C=O bond in *ortho* substituent to 1-(2-pyridyl)-2-(pentamethyldisilanyl)ethyne inserts intramolecularly into Si–C bond of the silacyclopropene or Si=C bond of 1-silaallene intermediates, we have examined the photolysis of **2a** and **2b** and we describe, in this paper, detailed photoreactions of **2a** and **2b** in various solvents.

2. Experimental

2.1. General methods

All reactions were carried out under an atmosphere of dry nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on

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Bruker AM-300 and Bruker AC-200 spectrometers with chemical shifts being referenced against TMS as an internal standard or the signal of the solvent CDCl$_3$. UV absorption spectra were recorded on a Hewlett-Packard 8453 spectrophotometer. Mass spectra were determined at 70 eV with a Hewlett-Packard 5985A GC–MS by the electron impact (EI) method. FT-IR spectra were recorded on a Bomem MB-100 spectrometer in KBr pellets and NaCl cell. High-performance liquid chromatography was performed on a Waters Associates Model 244 liquid chromatograph (Mildford, MA) equipped with a Model 6000A solvent delivery system, Model 440 UV absorbance detector fixed at 254 nm, and Model U6K universal injector. Lichrosorb SI-60 column was used for preparative analyses. Thin layer chromatography (TLC) was performed on Sigma–Aldrich pre-coated silica gel F$_{254}$ aluminum foils. Purification of the reaction products was carried out by flash column chromatography using a glass column dry packed with silica gel (230–400 mesh ASTM). Benzene was distilled from CaH$_2$ before use. NEt$_3$ was distilled from CaH$_2$ and stored over KOH pellets. Solvents of reagent grade for chromatography were used without further purification. Spectroscopic grade solvents were used for HPLC and UV absorption spectra.

2.2. Synthesis of 3-acetoxy-2-bromopyridine 1a

A solution of 2-bromo-3-pyridinol (0.5 g, 2.87 mmol) in N,N-dimethylformamide (5 ml) was added to a solution of NaH (75.8 mg, 3.16 mmol) in DMF (10 ml) at room temperature under nitrogen atmosphere. Acetyl chloride (0.3 ml, 4.3 mmol) was added dropwise to the resulting solution and the mixture was stirred at 25 °C for 2 h. Water (20 ml) was added to the solution and was extracted with ethyl acetate (3× 15 ml). The combined ethyl acetate solution was washed with water (20 ml), brine (20 ml) and dried (MgSO$_4$), and concentrated in vacuo to give the crude product. Flash column chromatography with n-hexane/ethyl acetate (3:1 v/v) as an eluent gave 1a (0.57 g, 92% yield) as a colorless oil; ^{1}H NMR (CDCl$_3$, 600 MHz), δ_H (ppm): 2.30 (3H, s), 7.24 (1H, dd, $J = 8.0$, 4.5 Hz), 7.41 (1H, dd, $J = 8.0$, 1.5 Hz), 8.20 (1H, dd, $J = 4.5$, 1.5 Hz); ^{13}C NMR (CDCl$_3$, 150 MHz), δ_C (ppm): 21.1, 123.9, 132.2, 136.8, 145.9, 147.4, 168.3; UV (CH$_2$Cl$_2$), λ_{max} (nm): 269; FT-IR (NaCl, cm^{-1}): 3061.7, 2935.8, 1771.9, 1570.3, 1408.8, 1192.5, 895.9; MS (70 eV), m/z: 215 (M^+); HRMS (M^+) for C$_7$H$_6$BrNO$_2$: calcd., 214.9582; found, 214.9566.

2.3. Synthesis of 3-methoxycarbonylmethoxy-2-bromopyridine 1b

A solution of 2-bromo-3-pyridinol (0.5 g, 2.87 mmol) in N,N-dimethylformamide (5 ml) was added to a solution of NaH (75.8 mg, 3.16 mmol) in DMF (10 ml) at room temperature under nitrogen atmosphere. Methyl bromoacetate (0.41 ml, 4.3 mmol) was added dropwise to the resulting solution and the mixture was stirred at 40 °C for 4 h. Water

(30 ml) was added to the solution and was extracted with ethyl acetate (3× 15 ml). The combined ethyl acetate solution was washed with water (20 ml), brine (20 ml) and dried (MgSO$_4$), and concentrated in vacuo to give the crude product. Flash column chromatography with n-hexane/ethyl acetate (1:1 v/v) as an eluent gave 1b (0.53 g, 75% yield); ^{1}H NMR (CDCl$_3$, 600 MHz), δ_H (ppm): 3.74 (3H, s), 4.69 (2H, s), 7.05 (1H, dd, $J = 8.1$, 1.2 Hz), 7.15 (1H, dd, $J = 8.1$, 4.7 Hz), 7.96 (1H, dd, $J = 4.7$, 1.2 Hz); ^{13}C NMR (CDCl$_3$, 150 MHz), δ_C (ppm): 52.8, 66.4, 121.0, 123.8, 133.5, 142.9, 151.9, 168.5; UV (CH$_2$Cl$_2$), λ_{max} (nm): 280, 230; FT-IR (NaCl, cm^{-1}): 3064.7, 2959.9, 1751.5, 1566.3, 1458.6, 1129.4, 797.7 cm^{-1}; MS (70 eV), m/z: 245 (M^+); HRMS (M^+) for C$_8$H$_8$BrNO$_3$: calcd., 244.9688; found, 244.9686.

2.4. Synthesis of 1-(3-acetoxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne 2a

To a deaerated solution of 3-acetoxy-2-bromopyridine 1a (0.5 g, 2.33 mmol), bis(triphenylphosphine)palladium dichloride (16.2 mg, 0.023 mmol) and copper(I) iodide (4.4 mg, 0.023 mmol) in anhydrous triethylamine (10 ml) were added dropwise pentamethyldisilanylethyne (0.40 g, 2.56 mmol) at room temperature. The reaction mixture was heated at 40 °C for 6 h. To this solution saturated ammonium chloride solution (20 ml) was added and the reaction mixture was extracted with ethyl acetate (3× 20 ml). The combined ethyl acetate solution was washed with H$_2$O (10 ml), brine (10 ml), and dried (MgSO$_4$), and concentrated in vacuo to give the crude product. Flash column chromatography with n-hexane/ethyl acetate (3:1 v/v) as an eluent gave 2a (0.38 g, 56% yield); ^{1}H NMR (CDCl$_3$, 600 MHz), δ_H (ppm): 0.16 (9H, s), 0.29 (6H, s), 2.34 (3H, s), 7.27 (1H, dd, $J = 8.2$, 4.6 Hz), 7.45 (1H, dd, $J = 8.2$, 1.2 Hz), 8.45 (1H, dd, $J = 4.6$, 1.2 Hz); ^{13}C NMR (CDCl$_3$, 150 MHz), δ_C (ppm): -2.89, -2.19, 21.3, 100.7, 101.5, 123.8, 130.4, 137.7, 147.5, 149.3, 168.5; UV (CH$_2$Cl$_2$), λ_{max} (nm): 288, 247; FT-IR (NaCl, cm^{-1}): 3060.1, 2961.1, 2165.4, 1771.5, 1569.7, 1408.5, 1192.1, 895.5; MS (70 eV), m/z: 291 (M^+); HRMS (M^+) for C$_{14}$H$_{21}$NO$_2$Si$_2$: calcd., 291.1111; found, 291.1101.

2.5. Synthesis of 1-(3-methoxycarbonylmethoxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne 2b

To a deaerated solution of 3-methoxycarbonylmethoxy-2-bromopyridine 1b (0.5 g, 2.04 mmol), bis(triphenylphosphine)palladium dichloride (14.3 mg, 0.020 mmol) and copper(I) iodide (3.9 mg, 0.020 mmol) in anhydrous triethylamine (10 ml) were added dropwise pentamethyldisilanylethyne (0.35 g, 2.25 mmol) at room temperature. The reaction mixture was heated at 40 °C for 4 h. To this solution saturated ammonium chloride solution (20 ml) was added and the reaction mixture was extracted with ethyl acetate (3× 20 ml). The combined ethyl acetate solution was washed with H$_2$O (10 ml), brine (10 ml), and dried (MgSO$_4$), and

concentrated in vacuo to give the crude product. Flash column chromatography with n-hexane/ethyl acetate (1:1 v/v) as an eluent gave **2b** (0.34 g, 52% yield); ^{1}H NMR (CDCl$_3$, 600 MHz), δ_H (ppm): 0.17 (9H, s), 0.30 (6H, s), 3.79 (3H, s), 4.72 (2H, s), 7.15 (2H, m), 8.23 (1H, d, $J = 3.4$ Hz); ^{13}C NMR (CDCl$_3$, 150 MHz), δ_C (ppm): -2.84, -2.15, 52.7, 66.7, 100.4, 102.4, 121.4, 123.8, 134.8, 143.6, 156.2, 169.0; UV (CH$_2$Cl$_2$), λ_{max} (nm): 304, 249; FT-IR (NaCl, cm^{-1}): 2959.9, 2158.9, 1764.4, 1575.2, 1434.3, 1128.4, 802.3; MS (70 eV), m/z: 321 (M^+); HRMS (M^+) for C$_{15}$H$_{23}$NO$_3$Si$_2$: calcd., 321.1216; found, 321.1211.

2.6. Irradiation of 1-(3-acetoxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne 2a in benzene

Deaerated solution (5×10^{-4} M) of 1-(3-acetoxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **2a** (145 mg) in benzene (1 l) was irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 300 nm lamps. After irradiation for 0.5 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts **5** and **6** [31] were isolated in 14.0 mg (12% yield) and 14.3 mg (15% yield) by column chromatography with n-hexane/ethyl acetate (3:1 v/v) as an eluent followed by normal phase HPLC using n-hexane/ethyl acetate (1:1 v/v) as an eluent. Compound **5**: ^{1}H NMR (CDCl$_3$, 600 MHz), δ_H (ppm): 0.25 (9H, s), 2.33 (3H, s), 7.26 (1H, dd, $J = 8.2$, 4.5 Hz), 7.43 (1H, dd, $J = 8.2$, 1.1 Hz), 8.43 (1H, dd, $J = 4.5$, 1.1 Hz); ^{13}C NMR (CDCl$_3$, 150 MHz), δ_C (ppm): 0.034, 21.2, 99.4, 101.1, 124.1, 130.4, 137.6, 147.6, 149.5, 168.5; UV (CH$_2$Cl$_2$), λ_{max} (nm): 285, 246; FT-IR (NaCl, cm^{-1}): 3060.6, 2960.7, 2166.8, 1775.6, 1584.3, 1433.4, 1194.8, 891.0; MS (70 eV), m/z: 233 (M^+); HRMS (M^+) for C$_{12}$H$_{15}$NO$_2$Si: calcd., 233.0872; found, 233.0869.

2.7. Irradiation of 1-(3-acetoxy-2-pyridyl)-2-(pentamethyl-disilanyl)ethyne 2a in benzene in the presence of water

Deaerated solution (5×10^{-4} M) of 1-(3-acetoxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **2a** (145 mg) and water (0.5 ml) in benzene (1 l) was irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 300 nm lamps. After irradiation for 1.5 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts **5**, **7–9**, and **11** were isolated in 5.8 mg (5% yield), 18.5 mg (12% yield), 18.8 mg (16% yield), 14.1 mg (12% yield), and 15.5 mg (10% yield), respectively, by column chromatography with n-hexane/ethyl acetate (3:1 v/v) as an eluent followed by normal phase HPLC using n-hexane/ethyl acetate (1:1 v/v) as an eluent. Compound **7**: ^{1}H NMR (CDCl$_3$, 600 MHz), δ_H (ppm): 0.10 (9H, s), 0.35 (6H, s), 2.34 (3H, s), 7.25 (1H, dd, $J = 8.0$, 5.0 Hz), 7.43 (1H, dd, $J = 8.0$, 1.5 Hz), 7.74 (1H, s), 8.45 (1H, dd, $J = 5.0$, 1.5 Hz); ^{13}C NMR (CDCl$_3$, 150 MHz), δ_C (ppm): 0.83, 1.64, 21.0, 123.5, 130.2, 145.6, 146.6, 147.4, 150.5, 151.8, 168.8; UV (CH$_2$Cl$_2$), λ_{max} (nm): 293, 247; FT-IR (NaCl,

cm^{-1}): 3325.8, 3066.6, 2958.2, 1770.3, 1590.1, 1430.2, 1248.3, 845.9; MS (70 eV), m/z: 309 (M^+); HRMS (M^+) for C$_{14}$H$_{23}$NO$_3$Si$_2$: calcd., 309.1216; found, 309.1228.

Compound **8**: ^{1}H NMR (CDCl$_3$, 600 MHz), δ_H (ppm): 0.16 (9H, s), 2.36 (3H, s), 6.17 (1H, d, $J = 14.5$ Hz), 7.21 (1H, dd, $J = 8.0$, 4.5 Hz), 7.30 (1H, d, $J = 14.5$ Hz), 7.41 (1H, dd, $J = 8.0$, 1.5 Hz), 8.44 (1H, dd, $J = 4.5$, 1.5 Hz); ^{13}C NMR (CDCl$_3$, 150 MHz), δ_C (ppm): 0.81, 21.2, 123.1, 130.3, 137.0, 140.6, 145.1, 145.9, 148.9, 169.1; UV (CH$_2$Cl$_2$), λ_{max} (nm): 294, 248; FT-IR (NaCl, cm^{-1}): 3061.3, 2953.6, 1771.9, 1586.6, 1434.1, 1198.8, 855.1; MS (70 eV), m/z: 235 (M^+); HRMS (M^+) for C$_{12}$H$_{17}$NO$_2$Si: calcd., 235.1029; found, 235.1036.

Compound **9**: ^{1}H NMR (CDCl$_3$, 600 MHz), δ_H (ppm): 0.20 (9H, s), 2.39 (3H, s), 7.05 (1H, d, $J = 19$ Hz), 7.23 (1H, dd, $J = 8.5$, 4.5 Hz), 7.29 (1H, d, 19 Hz), 7.45 (1H, dd, $J = 8.5$, 1.5 Hz), 8.50 (1H, dd, $J = 4.5$, 1.5 Hz); ^{13}C NMR (CDCl$_3$, 150 MHz), δ_C (ppm): -1.23, 21.1, 123.3, 130.9, 137.9, 144.7, 145.8, 147.2, 147.9, 169.1; UV (CH$_2$Cl$_2$), λ_{max} (nm): 294, 247; FT-IR (NaCl, cm^{-1}): 3061.0, 2953.3, 1771.2, 1583.9, 1433.1, 1197.6, 856.8; MS (70 eV), m/z: 235 (M^+); HRMS (M^+) for C$_{12}$H$_{17}$NO$_2$Si: calcd., 235.1029; found, 235.1006.

Compound **11**: ^{1}H NMR (CDCl$_3$, 600 MHz), δ_H (ppm): 0.18 (9H, s), 0.31 (6H, s), 2.23 (3H, s), 6.41 (1H, s), 7.16 (1H, dd, $J = 8.0$, 5.0 Hz), 7.37 (1H, dd, $J = 8.0$, 1.5 Hz), 8.43 (1H, dd, $J = 5.0$, 1.5 Hz); ^{13}C NMR (CDCl$_3$, 150 MHz), δ_C (ppm): 1.72, 2.09, 21.1, 121.8, 130.5, 143.3, 145.9, 146.3, 148.6, 153.3, 168.9; UV (CH$_2$Cl$_2$), λ_{max} (nm): 292, 247; FT-IR (NaCl, cm^{-1}): 3324.5, 3062.9, 2956.6, 1752.3, 1589.1, 1429.1, 1200.9, 850.5; MS (70 eV), m/z: 309 (M^+); HRMS (M^+) for C$_{14}$H$_{23}$NO$_3$Si$_2$: calcd., 309.1216; found, 309.1219.

2.8. Irradiation of 1-(3-acetoxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne 2a in methanol

A solution (5×10^{-4} M) of 1-(3-acetoxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **2a** (145 mg) in methanol (1 l) was deaerated by nitrogen purging for 1 h and irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 300 nm lamps. After irradiation for 1 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts **5**, **8–10**, and **12** were isolated in 11.7 mg (10% yield), 15.3 mg (13% yield), 5.9 mg (5% yield), 19.4 mg (12% yield), and 7.2 mg (9% yield), respectively, by column chromatography with n-hexane/ethyl acetate (3:1 v/v) as an eluent followed by normal phase HPLC using n-hexane/ethyl acetate (1:1 v/v) as an eluent. Compound **10**: ^{1}H NMR (CDCl$_3$, 600 MHz), δ_H (ppm): 0.10 (9H, s), 0.31 (6H, s), 2.34 (3H, s), 3.47 (3H, s), 7.25 (1H, dd, $J = 8.0$, 4.5 Hz), 7.43 (1H, dd, $J = 8.0$, 1.5 Hz), 7.71 (1H, s), 8.46 (1H, dd, $J = 4.5$, 1.5 Hz); ^{13}C NMR (CDCl$_3$, 150 MHz), δ_C (ppm): -0.67, 1.95, 21.0, 50.6, 123.5, 130.2, 145.9, 146.5, 147.2, 150.4, 151.9, 168.8; UV (CH$_2$Cl$_2$), λ_{max} (nm): 292, 247; FT-IR (NaCl, cm^{-1}): 3060.6, 2955.7, 1773.2,

1586.4, 1430.9, 1248.8, 854.6; MS (70 eV), m/z: 323 (M^+); HRMS (M^+) for $C_{15}H_{25}NO_3Si_2$: calcd., 323.1373; found, 323.1369. Compound **12**: ^{1}H NMR (CDCl$_3$, 600 MHz), δ_H (ppm): 2.39 (3H, s), 3.37 (1H, s), 7.35 (1H, dd, $J = 8.5$, 4.5 Hz), 7.50 (1H, dd, $J = 8.5$, 1.5 Hz), 8.50 (1H, dd, $J = 4.5$, 1.5 Hz); ^{13}C NMR (CDCl$_3$, 150 MHz), δ_C (ppm): 21.1, 78.6, 82.3, 124.4, 130.4, 136.6, 147.5, 149.5, 168.6; UV (CH$_2$Cl$_2$), λ_{max} (nm): 279, 236; FT-IR (NaCl, cm^{-1}): 3060.6, 2955.9, 2114.3, 1768.0, 1585.6, 1435.2, 1195.7, 849.0; MS (70 eV), m/z: 161 (M^+); HRMS (M^+) for $C_9H_7NO_2$: calcd., 161.0477; found, 161.0466.

2.9. Irradiation of 1-(3-methoxycarbonylmethoxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne 2b in benzene

Deaerated solution (5×10^{-4} M) of 1-(3-methoxy-carbonylmethoxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne **2b** (160 mg) in benzene (1 l) was irradiated in a Rayonet photochemical reactor, model RPR-208, equipped with RUL 300 nm lamps. After irradiation for 1 h, the resulting photoreaction mixture was concentrated in vacuo. The photoadducts **14** and **15** were isolated in 14.5 mg (11% yield) and 44.9 mg (28% yield) by column chromatography with n-hexane/ethyl acetate (10:1 v/v) as an eluent followed by normal phase HPLC using n-hexane/ethyl acetate (5:1 v/v) as an eluent. Compound **14**: ^{1}H NMR (CDCl$_3$, 600 MHz), δ_H (ppm): 0.19 (9H, s), 3.71 (3H, s), 4.67 (2H, s), 7.10 (2H, m), 8.13 (1H, d, $J = 4$ Hz); ^{13}C NMR (CDCl$_3$, 150 MHz), δ_C (ppm): −0.13, 52.4, 66.2, 100.0, 100.6, 120.9, 123.9, 133.9, 143.1, 155.9, 168.6; UV (CH$_2$Cl$_2$), λ_{max} (nm): 301, 245; FT-IR (NaCl, cm^{-1}): 2957.5, 2164.6, 1760.4, 1578.3, 1437.7, 1250.4, 811.2; MS (70 eV), m/z: 263 (M^+); HRMS (M^+) for $C_{13}H_{17}NO_3Si$: calcd., 263.0978; found, 263.0969. Compound **15**: UV (CH$_2$Cl$_2$), λ_{max} (nm): 318, 246; FT-IR (NaCl, cm^{-1}): 2953.9, 1555.2, 1430.9, 1279.6, 1031.7, 882.9; MS (70 eV), m/z: 321 (M^+); HRMS (M^+) for $C_{15}H_{23}NO_3Si_2$: calcd., 321.1216; found, 321.1270.

3. Results and discussion

The starting 1-(3-acetoxy or methoxycarbonylmethoxy-2-pyridyl)-2-(pentamethyldisilanyl)ethynes **2a** and **2b**, respectively, were prepared by the reaction of 3-substituted-oxy-2-bromopyridines **1a** and **1b** with pentamethyldisilanylethyne
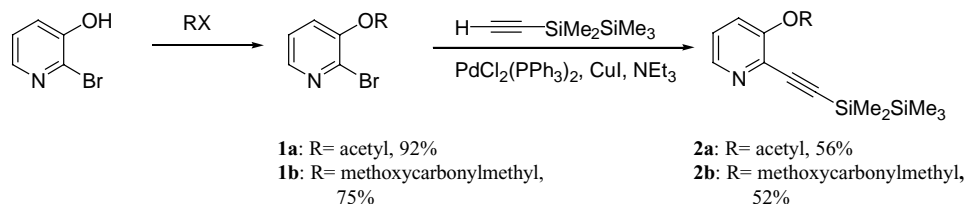
in the presence of bis(triphenylphosphine)palladium dichloride and copper(I) iodide in triethylamine (Scheme 1).

3.1. Photoreaction of 1-(3-acetoxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne 2a

To investigate whether or not the C=O bond in *ortho* substituent (acetoxy group) in **2a** inserts intramolecularly into Si–C bond of silacyclopropene intermediate **3** or Si=C bond of 1-silaallene intermediate **4**, we carried out the photolysis of **2a**.

Irradiation of **2a** in deaerated benzene with 300 nm UV light provided two photoproducts **5** (12% yield) and **6** (15% yield) along with some products of unknown structure as shown in Scheme 2 but the expected photoinduced intramolecular cycloaddition products via silacyclopropene or 1-silaallene intermediates were not detected. It is thought that the compounds **5** or **6** were formed from the liberation of dimethylsilylene or acetyl species from the silacyclopropene intermediate **3**. In the case of the photolysis of 1-(*ortho*-acetoxyphenyl)-2-pentamethyldisilanylethyne in benzene [30], two photo-Fries rearrangement products and a photoproduct formed from the liberation of dimethylsilylene species in the silacyclopropene intermediate were obtained but the expected intramolecular cycloaddition photoproducts were also not formed. In the case of the photolysis of **2a**, even the photo-Fries rearrangement did not occur. On the other hand, the photolysis of 1-(3-hydroxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne in benzene [31] gave the novel cycloaddition photoproducts by the concerted intramolecular cycloaddition reaction between the hydroxy group in *ortho* substituent and Si–C bond of silacyclopropene intermediate formed, indicating that the hydroxy group is much more reactive than the acetoxy group as *ortho* substituent to 1-(2-pyridyl)-2-(pentamethyldisilanyl)ethyne.

To investigate the photoreaction of **2a** in the presence of a trapping agent, the photolysis of **2a** in water was carried out. Irradiation of **2a** in deaerated benzene in the presence of water as a trapping agent with 300 nm UV light afforded the photoproducts **5**, **7**–**9**, and **11** (5, 12, 16, 12, and 10% yields, respectively) but the expected cycloaddition photoproducts were also not obtained. It is thought that the photoproducts **7** or **11** were formed from the reaction of the silacyclopropene **3** or 1-silaallene intermediate **4** with water, respectively, and the compounds **8** and **9** were formed

1a: R= acetyl, 92%
1b: R= methoxycarbonylmethyl, 75%

2a: R= acetyl, 56%
2b: R= methoxycarbonylmethyl, 52%

Scheme 1.

Scheme 2.

from the hydrolysis (proto-desilylation) of the photoproduct **7** in the presence of water. The structure of photoisomer **8** could be distinguished from that of **9** on the basis of the ^{1}H NMR spectra of the isomer pairs. The vinylic protons in **8** show *cis* coupling constant ($J = 14.5$ Hz), whereas those in **9** show *trans* coupling constant ($J = 19$ Hz) and two doublets from the vinylic protons of **8** were observed at 6.17 and 7.21 ppm, while its isomer **9** showed the two doublets at 7.05 and 7.29 ppm. The structures of **7** and **11** were confirmed by comparison with the reported results of the photoreaction of 1-(2-pyridyl)-2-(pentamethyldisilanyl)ethyne in benzene in the presence of water [21]. In particular, two singlets from the vinylic protons of **7** and **11** were observed at 7.74 and 6.41 ppm, respectively, indicating that the photoproducts **7** and **11** have an *E*-configuration.

Irradiation of **2a** in deaerated methanol with 300 nm UV light gave the photoproducts **5**, **8–10**, and **12** (10, 13, 5, 12, and 9% yield, respectively) along with some products of unknown structure shown in Scheme 2. In this case, the expected intramolecular cycloaddition photoproducts were also not obtained and the regioselective methanol addition photoproduct **10** similar to the photoproduct formed from the photoreaction of 1-(2-pyridyl)-2-(pentamethyldisilanyl)ethyne in methanol [21] was obtained. In the case of the photoreactions of 1-(*n*-pyridyl)-2-(pentamethyldisilanyl)ethynes (*n* = 2, 3, or 4) in methanol or benzene [21], only the photoproducts formed from the silacyclopropene intermediate were obtained in methanol but the photoproducts formed from both the silacyclopropene and 1-silaallene intermediates were obtained in benzene. And, it is thought that compounds **8** and **9** were also formed from the hydrolysis (proto-desilylation) of the photoproduct **10** in the presence of methanol and the photoproduct **12** was, probably, formed through C–Si bond cleavage in the photoexcited state of **2a** [17,27].

3.2. Photoreaction of 1-(3-methoxycarbonylmethoxy-2-pyridyl)-2-(pentamethyldisilanyl)ethyne 2b

To investigate the reactivity of methoxycarbonylmethoxy group instead of acetoxy group as *ortho* substituent to 1-(2-pyridyl)-2-(pentamethyldisilanyl)ethyne, we carried out the photolysis of **2b** in benzene.

Irradiation of **2b** in deaerated benzene with 300 nm UV light afforded a novel intramolecular cycloaddition photoproduct **15** (28% yield) in addition to **14** (11% yield) along with some decomposition products of unknown structure as shown in Scheme 3. The formation of product **15** can be rationalized in terms of the initial formation of silacyclopropene intermediate **13** upon irradiation followed by the concerted intramolecular cycloaddition reaction between the C=O bond in *ortho* substituent and Si–C bond of silacyclopropene formed. In the case of the photolysis of 1-(*ortho*-methoxycarbonylmethoxyphenyl)-2-(pentamethyl-disilanyl)ethyne in benzene [23], the novel intramolecular cycloaddition product similar to **15** via silacyclopropene intermediate was also obtained but the photoproducts via 1-silaallene intermediate were not detected in both cases. Liberation of dimethylsilylene species from the silacyclopropene intermediate **13** resulted in the formation of **14**.

The structure of the photoproduct **15** was determined by various spectroscopic methods including [1]H–[1]H and [1]H–[13]C correlation spectroscopy (COSY), HMBC, nuclear overhauser and exchange spectroscopy (NOESY) (Table 1). The [1]H–[1]H and [1]H–[13]C correlation spectroscopy (COSY) spectra of **15** were carried out to identify the protons directly attached to the individual carbons. According to the correlated peaks in **15**, we have been able to identify the pairs of carbons and directly bonded protons as shown in Table 1. In order to determine the location of the quaternary carbons, the HMBC spectrum of **15** was taken. The presence of the cross-peaks due to the vicinal coupling between
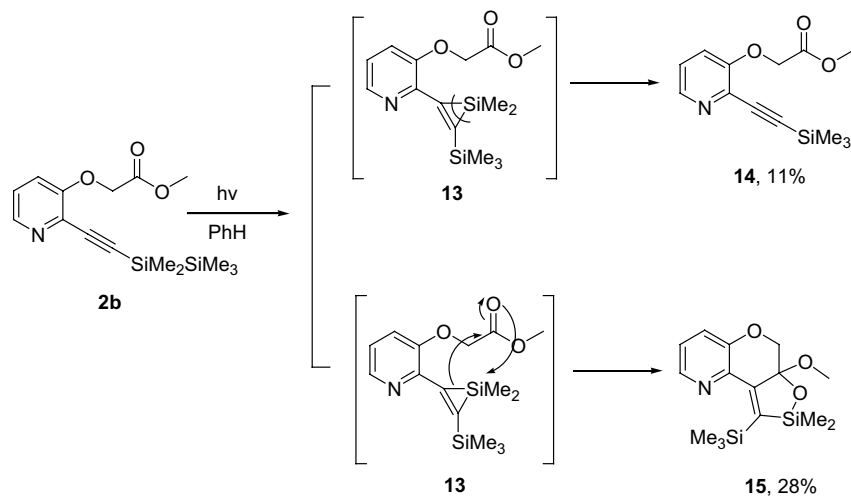
Scheme 3.

Table 1
^{1}H NMR (600 MHz), ^{13}C NMR (150 MHz), and HMBC data for photoproduct **15** in CDCl$_3$[a]

Position	δ_C (ppm)	Multiplicities, M[b]	δ_H (ppm)	Integrated intensity, I	Multiplicities, M	J_{H-H} (Hz)	HMBC[c]
1	124.9	d	7.21	1H	dd	8.5 (J_{1H-2H}), 1.5 (J_{1H-3H})	H3
2	124.5	d	7.15	1H	dd	8.5 (J_{2H-1H}), 4.5 (J_{2H-3H})	
3	141.9	d	8.23	1H	dd	4.5 (J_{3H-2H}), 1.5 (J_{3H-1H})	H1
4	139.5	s					H1
5	151.7	s					H2, H6
6α	72.4	t	3.93	1H	d	11 ($J_{6αH-6βH}$)	
6β	72.4	t	4.51	1H	d	11 ($J_{6βH-6αH}$)	
7	102.4	s					H6, H10
8	156.5	s					H6
9	141.0	s					H11, H12
10	49.8	q	3.20	3H	s		
11α	1.20	q	0.31	3H	s		
11β	0.64	q	0.50	3H	s		
12	1.14	q	0.26	9H	s		

[a] All these assignments were confirmed by ^{1}H–^{1}H and ^{1}H–^{13}C COSY and NOESY, HMBC spectra.

[b] Determined by DEPT spectrum.

[c] Protons correlated to carbon resonances in ^{13}C column.

the protons of C**6** and the quaternary carbon C**5** and C(8) in **15** showed the connectivity of the carbon C**6** to the double bond (C$_8$=C$_9$) and the pyridine moiety of **15**. In the same manner, the presence of the cross-peaks due to the vicinal coupling between the protons of C(11) and C(12) and the quaternary carbon C(9) in **15** showed the connectivity of the carbon C(9) to the trimethylsilyl and the dimethylsilyl groups in **15**. The 3D structure of **15** was determined by a nuclear overhauser and exchange spectroscopy (NOESY). In particular, the presence of the cross-peak between the protons of C(11) and the protons of C(12) in **15** showed the close proximity of the protons of C(11) to the protons of C(12) indicating that these protons are located on the same side of the molecule. Thus, the skeletal structure of **15** was unambiguously established as shown in Fig. 1.

In conclusion, the photolysis of **2a** in various solvent systems provided various photoproducts including the reduction product and the products formed from the reaction of silacyclopropene or 1-silaallene intermediates with trapping agents but the expected photoinduced intramolecular cycloaddition products via silacyclopropene or 1-silaallene intermediates were not obtained. In the case

of benzene solvent, even the photo-Fries rearrangement products were not obtained unlike the reported results for 1-(*ortho*-acetoxyphenyl)-2-(pentamethyldisilanyl)ethyne [30]. However, irradiation of **2b** in benzene gave the expected cycloaddition photoproduct **15** via silacyclopropene intermediate **13**. The C=O bond in methoxycarbonyl-methoxy group as *ortho* substituent to 1-(2-pyridyl)-2-(pentamethyldisilanyl)ethyne inserts intramolecularly into Si–C bond of silacyclopropene intermediate **13**, while that in acetoxy group did not react with Si–C bond of silacyclopropene intermediate **3**.

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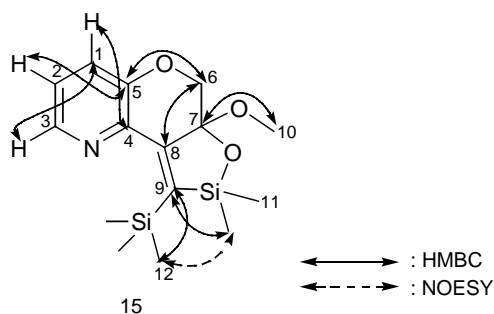

Fig. 1. Important correlations observed in HMBC and NOESY spectra of photoproduct **15**.

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